Acidity of SiO₂ -Supported Metal Oxides in the Presence of H₂O Using the Adsorption Equilibrium Infrared Spectroscopy Method: 1. Adsorption and Coadsorption of NH₃ and H₂O on SiO₂

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**Acidity of SiO₂ supported metal oxides in the presence of
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ABSTRACT

The present study is dedicated to the characterization (identification, heats of adsorption and coverages) of the adsorbed species formed by the adsorption and coadsorption of NH_3 and H_2O on two SiO_2 solids. The Adsorption Equilibrium InfraRed spectroscopy (AEIR) which allowed (a) to show that NH_3 and H_2O are mostly adsorbed on free SiOH groups via H-bonds and (b) to determine their individual heats of adsorption: 53 kJ/mol and 49 kJ/mol whatever their coverages (Langmuir adsorption model) for $\text{NH}_{3\text{ads}}$ and $\text{H}_{2\text{Oads}}$, respectively. These values consistent with microcalorimetry literature data explain that their coverages are decreased upon $\text{NH}_3\text{-H}_2\text{O}$ co-adsorption considering a competitive Langmuir model. However, the Temperature Programmed Adsorption Equilibrium (TPAE) procedure achieved from MS data indicated that a minor amount of other NH_3 species (not detected using FTIR) are more strongly adsorbed and that hydrolysis of SiOSi siloxane by H_2O could occur in parallel. $\text{NH}_3\text{-H}_2\text{O}$ coadsorption leads to formation of NH_4^+ species which involves H_2O adsorbed species. Both NH_3 and H_2O are not adsorbed above 450 K which means that the SiO_2 contribution to the characterization of the acidity of metal oxides catalysts supported on SiO_2 using NH_3 as probe molecule in the presence of H_2O is negligible above this temperature.

INTRODUCTION

The surface properties of silica which can be synthesized by different routes are used in different industrial processes such as adsorption (including chromatography), membrane separation and heterogeneous catalysis and therefore have been studied since a long time.¹⁻⁵

The present study concerns the use of SiO_2 as support of metal oxides which are of interest as catalysts in different reactions⁶ involving acidic sites particularly $\text{TiO}_2/\text{SiO}_2$ compounds for the dehydration/isomerization of bio-sourced isobutanol for the production of butenes^{7,8}. The understanding of the role of these supported catalysts imposes the characterisation of their surface acidic sites particularly using adsorption of basic molecules such as NH_3 . The identification of the different adsorbed species i.e. molecular NH_3 and NH_4^+ species reveals the presence of Lewis and/or Brønsted acidic sites, respectively whereas the measurement of their individual heats of adsorption provides the evaluation of their strength. Moreover, as SiO_2 supported metal oxide catalysts can be operant in the presence of a large amount of H_2O (either as reactant or product) the impact of the $\text{NH}_3\text{-H}_2\text{O}$ coadsorption must be considered in these characterizations in line with the concept of water-tolerant acidic sites.⁹⁻¹¹ Such impact is investigated in Part 2 of the present study¹² dedicated to the characterization of the acidic sites of two $\text{TiO}_2/\text{SiO}_2$ catalysts. How may the support contribute to these measurements constitutes a key point and it is the aim of this Part 1 which concerns two synthetic SiO_2 solids.

SiO_2 surface is composed of hydroxylated patches (adjacent SiOH groups interacting by H-bonding and isolated 'free' ones) alternating with patches of siloxane (SiOSi) bridges which are more or less reactive depending on their strain state.^{2,13} The nature, amount, and geometrical arrangement of silanol groups and siloxane bridges determine the surface properties of SiO_2 in particular hydrophilicity/hydrophobicity.² For instance, in ambient atmosphere (hydrated state) all the surface silanols are hydrogen bonded to adjacent silanols

and water molecules while after a drying at 200 °C, half of geminal and isolated silanols remains H-bonded.¹⁴

The nature of the adsorption sites for H₂O and NH₃ on SiO₂ has been the subject of considerable controversy.¹⁵ For instance, Hertl and Hair¹⁶ reported that H₂O interacts specifically with the free OH groups whereas Fubini et al.^{13,17} reported that it absorbs both on hydroxylated patches (adjacent silanols) via two hydrogen bonds (named H-bonds) and on free silanols in dehydroxylated region via one H-bond. In fact, the first water molecules might adsorb via two H-bonds on close neighbouring but non-interacting surface silanols.¹⁸ Therefore, even if different adsorption modes take place, the adsorption sites can be considered as the free (without H-bonding) silanols which are not necessarily isolated in dehydroxylated region. Note that H₂O water can act both as acceptor and as donor.²

Similar ambiguity can be found upon adsorption of NH₃ on SiO₂. FTIR studies of modifications of $\nu(\text{O-H})$ stretching bands showed that NH₃ adsorption proceeds via H-bonding between the electron pair of the N atom and the H-donor SiO-H species according to a Langmuir adsorption model and no other process has been singled out.¹ However, an unspecific interaction not conspicuous in the IR spectra and described by a Henry-type adsorption isotherm was revealed by quantitative measurements.¹ Tsyganenko et al.¹⁹ reported that H-bonded ammonia molecule can also act as a donor of proton in one more H-bond with the oxygen atom of adjacent silanol groups. After saturation of these double sites which is energetically favourable, H-bond with isolated silanol groups should occur leading to a smaller $\nu(\text{O-H})$ shift. NH₃ was also reported to adsorb both on isolated SiOH and on H-bonded silanols located at the end of rings of silanols.^{17,20} In the latter case, co-operative effects were shown to break off the mutual interaction among silanols with an energetic cost that lowers the net heat released.^{20,21}

The measurement of the individual heats of adsorption of coadsorbed species, such as those formed by CO on supported metal particles and NH₃ on metal oxides cannot be easily

performed using conventional methods (i.e. microcalorimetry and temperature programmed desorption (TPD) methods). However, these parameters are key data in different fields particularly for either the modelling of coverage of the reactants of heterogeneous catalytic reactions²²⁻³⁰ considering the presence or not of competitive adsorption^{29,30} or the evaluation of the strength of acidic sites. This was the aims of two analytical methods named Adsorption Equilibrium InfraRed spectroscopy (AEIR) (its applications from 1998 have been reviewed recently)³¹ and Temperature Programmed Adsorption Equilibrium (TPAE).³² These methods provide (a) the experimental adsorption equilibrium coverage $\theta_{e_{X_{ads}}}(T_a, P_a)$ of an adsorbed species X_{ads} formed by a gas X for large ranges of adsorption temperature T_a and pressure P_a and (b) their mathematical modelling. These methods are based on the determination of $\theta_{e_{X_{ads}}}(T_a, P_a)$ during the increase T_a in quasi isobaric conditions by using a gas flow rate containing a partial pressure P_a of X. AEIR uses the evolution of an IR band characteristic of X_{ads} .³¹ TPAE (developed latter than AEIR as complementary method) is a revisit of TPD using a mass spectrometer as detector.³² The experimental curves $\theta_{e_{X_{ads}}}(T_a, P_a)$ are compared to adsorption models (Langmuir, Temkin) considering localized adsorbed species.^{31,32} This permits the measurements of the individual heats of adsorption of the different coadsorbed X_{ads} species (see more details below). It must be noted that due to the intrinsic and/or induced heterogeneity of the adsorption sites on numerous dispersed solids the AEIR/TPAE experimental data were often consistent with the Temkin model whereas the Langmuir one was operant in few cases for weakly adsorbed species.³¹ It has been shown that AEIR³¹ and TPAE³² experimental procedures maintain the adsorption equilibrium during the increase in T_a which presents different advantages as compared to methods such as microcalorimetry and TPD. For instance, this prevents the contribution of mass transfer limitations which are one of the difficulties using TPD.^{33,34}

In the present study, AEIR associated with TPAE is used for the characterisation of the adsorption sites of two SiO₂ solids for NH₃ or/and H₂O adsorption via the identification of the different adsorbed species (this is a revisit of literature data) and then the measurement of their heats of adsorption and the impacts of the coadsorption (those are mainly original data) in line with previous works dedicated to the selective catalytic reduction of NO by NH₃ on V₂O₅/WO₃/TiO₂ catalysts.³⁵⁻³⁹ This reveals the experimental conditions (T_a and P_a) for NH₃ and H₂O leading or not to a contribution of the support during the characterization of the acidic properties of two TiO₂/SiO₂ catalysts¹² by NH₃ in the absence and presence of H₂O.

METHODS

SiO₂ Samples

Two Commercial SiO₂ solids have been used in the present study: Grace (Davisil, 550 m².g⁻¹) and AEROSIL®200 (Evonik, 215 m².g⁻¹) (named SiO₂-G and SiO₂-A, respectively). Before adsorption of either NH₃ or H₂O or NH₃-H₂O mixtures, the solids were treated at ≈ 723 K on different analytical systems as follows: 0.5 h in O₂ and then 1 h in helium (helium was dried using cold traps at 77 K) and cooled in helium to room temperature (ca 300 K). Different experiments were performed on the same sample which was treated each time as above before adsorption. The OH surface densities determined from TGA measurements were 2.7 and 0.8 OH.nm⁻² for SiO₂-G and SiO₂-A, respectively after pre-treatment at 723 K.

IR Cell in Transmission Mode.

FTIR measurements were performed with a Nicolet 6700 spectrometer (ThermoScientific) using a homemade stainless steel IR cell reactor specially designed (a) to limit the gas phase contribution (its optical path was 2.2 mm) and (b) to record IR spectra in the room temperature-800 K range.⁴⁰ It allowed the study of adsorbed species on a compressed disk of solid (Φ= 1.8 cm, m≈ 40-80 mg) under gas flow rates (200 mL.min⁻¹ in the present study) of

gas mixtures at atmospheric pressure, such as $x\%$ $\text{NH}_3/y\%$ $\text{H}_2\text{O}/\text{He}$, with x and y in the ranges 0–1% and 0–3%, respectively selected using different switching valves. The amount of H_2O was fixed using a vaporizer/condenser system as described previously.³⁸ Only bands above 1250 cm^{-1} were observed in the present study because of the low IR transmission of SiO_2 samples and CaF_2 cell windows. After the pretreatment procedure at 723 K the duration of the cooling stage to RT was ≈ 1 h. This led to slight modifications of the $\nu(\text{O-H})$ bands of the analyzed solid which were considered in the present study. The evolutions of the bands of adsorbed species with an increase in the adsorption temperature T_a in isobaric conditions were exploited according to the AEIR procedure.³¹

Volumetric Measurements Using Mass Spectrometry.

The adsorption of NH_3 and its coadsorption with H_2O have been studied using an analytical system for transient experiments as described previously.⁴¹ Briefly, the composition (molar fractions X_i) of the gas mixture at the outlet of a quartz microreactor containing the pretreated solid (slightly compressed and then sized, weight range of 0.2–0.5 g, deposited on quartz wool) was determined by using a quadrupole mass spectrometer (Inficon, Transceptor CPM) during either switches between regulated gas flows (1 atm, flow rate in the range of 100–2000 mL/min) at a constant temperature or an increase in the temperature at a constant flow rate. The temperature was recorded via a stainless-steel K type thermocoax ($\Phi = 0.25\text{ mm}$) inserted in the sample of catalyst. All the stainless-steel tubes, before and after the microreactor until the source of the mass spectrometer, were heated to 373 K. After the pretreatment procedure, the time required to cool the sample from 723 to 300 K was ~ 4 min. The molar fractions provided the rate of either formation of a product j , $R_j = X_j M_F/m_s$ or consumption of a reactant i , $R_i = (X_{i,\text{in}} - X_i) M_F/m_s$ where M_F and m_s were the total molar flow rate and the weight of sample, respectively. $X_{i,\text{in}}$ was the molar fraction at the reactor inlet, X_j and X_i were the molar fraction of product j and reactant i , respectively at the outlet. The integration of R_j and R_i with

time on stream provided the total amount (in $\mu\text{mol/g}$ of catalyst) of production and consumption, respectively. For instance, the adsorption/desorption of NH_3 at T_a (i.e. 300 K) on pretreated SiO_2 was studied according to the following switches: $\text{He} \rightarrow 1\% \text{NH}_3/1\% \text{Ar/He}$ (Ar was used as tracer, $P_a = 1 \text{ kPa}$) providing the total amount of strongly and weakly adsorbed NH_3 species ($Q_{\text{NH}_3}(T_a, P_a)$). It was followed by a switch $1\% \text{NH}_3/1\% \text{Ar/He} \rightarrow \text{He}$ providing the amount of reversibly adsorbed species, which was confirmed by a new switch $\text{He} \rightarrow 1\% \text{NH}_3/1\% \text{Ar/He}$. Then, after the adsorption equilibrium at 300 K, the adsorption temperature T_a was increased progressively in the presence of the partial pressure of NH_3 ($P_{\text{NH}_3} = 1 \text{ kPa}$) to perform a TPAE experiment. Blank experiments with the empty reactor (with thermocouple and quartz wool) indicated the absence of NH_3 adsorption/decomposition at $300 \text{ K} \leq T \leq 723 \text{ K}$ (i.e. absence of a significant delay between Ar and NH_3). Similar experiments have been performed using $\text{NH}_3/\text{H}_2\text{O}/\text{Ar/He}$ gas mixtures. These experiments have been designed to prevent the impact of mass transfer limitations as described previously.³²

Heats of Adsorption of the Adsorbed NH_3 and H_2O Species Using the AEIR and TPAE Methods.

These measurements have been described in details in previous works^{31,32} and are briefly summarized: for the AEIR method^{31,35} the evolution of the intensity of a IR band characteristic of an adsorbed X_{ads} species (i.e. the $\delta_{\text{as}}(\text{NH}_3)$ IR band of molecularly adsorbed NH_3 species in the $1640\text{-}1600 \text{ cm}^{-1}$ range) with the increase in T_a in isobaric condition: $A(T_a, P_a)$, was used (Eq. S1 of the S.I) to follow the experimental evolution of the adsorption equilibrium coverage $\theta_{X_{\text{ads}}}(T_a, P_a)$ of X_{ads} . This curve was compared to theoretical curves using (a) classical adsorption model (in the present study either Langmuir (Eq. S2) or Temkin (Eq. S3) and (b) the mathematical expression of the adsorption coefficient provided by the statistical thermodynamic for localized adsorbed species (Eq. S4). The best fit between experimental and theoretical curves via the “minerr” function of Mathcad (nonlinear least square method) provides the heats of adsorption of the adsorbed species with an accuracy of $\pm 5 \text{ kJ/mol}$.

Moreover, an IR band can be due to the contribution of two adsorbed species: for instance, a $\delta_{\text{as}}(\text{NH}_3)$ band at $\approx 1600 \text{ cm}^{-1}$ observed after adsorption of NH_3 on TiO_2 based solids³⁵⁻³⁷ was common to two NH_3 species: $\text{NH}_{3\text{ads1}}$ and $\text{NH}_{3\text{ads2}}$ adsorbed on different Lewis (these two NH_3 species are identified by their respective $\delta_{\text{s}}(\text{NH}_3)$ bands below 1300 cm^{-1}). For this situation, it has been shown³⁵⁻³⁷ that Eq. S1 corresponds to the average coverage of the two adsorbed species which can be used to determine (a) their individual heats of adsorption and (b) their respective contributions to the intensity of the common IR band at saturation of the acidic Lewis sites (Eq. S5).

For the TPAE procedure³⁶ the experimental curve $\theta_{\text{e}}(T_{\text{a}}, P_{\text{a}})$ was obtained by using the net desorption rate of a gas: $R_{\text{i}}(t)$ due to the increase in the adsorption temperature T_{a} in quasi isobaric conditions according to Eq. S6. Then the heats of adsorption are obtained similarly to the AEIR method via Eq. S2-S5.

RESULTS AND DISCUSSION

Adsorption and Coadsorption of NH_3 and H_2O on SiO_2 -G using FTIR

Different SiO_2 solids (i.e Aerosil, Car-bo-sil, homemade) lead to the IR observation of a thin $\nu(\text{O-H})$ band at $3735\text{-}3750 \text{ cm}^{-1}$ particularly after dehydration/dehydroxylation either in inert gases or in vacuum at $T > 300 \text{ K}$ and there is a consensus on its assignment to free (non H-bonding) Si-OH groups which can be either isolated or non-interacting geminal or non-interacting vicinal.^{1,5,13,16,19,20,42-45} In fact, it was shown that this asymmetric band contains a second component located ca 5 cm^{-1} lower than the maximum attributed to very weakly interacting silanols.^{46,47}

The inset of Fig. 1 shows that this $\nu(\text{O-H})$ stretching band observed at 3734 cm^{-1} after the pretreatment procedure at 723 K (spectrum α) slightly raised, narrowed and shifted to 3742 cm^{-1} after the cooling stage to 300 K in helium (spectrum β). This is probably due to either the

impact of the temperature and casually the dissociative adsorption/hydrolysis of SiOSi bridges due to H₂O traces in the helium flow (see Ref. 35 and references therein). The broad shoulder at lower wavenumber which ranges to 3200 cm⁻¹ (Fig. S1) was due to $\nu(\text{O-H})$ stretching vibration of interacting vicinal (HOSi-O-SiOH) silanol groups remaining after dehydration at 723 K.^{13,16,20,42-44}

Figure 1. FTIR spectra recorded during adsorption of NH₃ (part A) and H₂O (part B) on SiO₂-G. **Part A:** Impact of the adsorption temperature T_a on the intensity of the $\delta_{as}(\text{NH}_3)$ band of NH_{3ads} species for 1% NH₃/He: (a)-(e) T_a = 300, 323, 343, 423, 473 K. **Inset:** Comparison of the $\nu(\text{O-H})$ bands of free OH groups after different pretreatments: (α) in helium at 723 K; (β) at 300 K after cooling from 723 K; (λ) at the adsorption equilibrium at 300 K using 1% NH₃/He. **Part B:** Impact of the adsorption temperature T_a on the intensity of the $\delta(\text{H}_2\text{O})$ band of H₂O_{ads} species for 3% H₂O/He: (a)-(g) T_a = 300, 323, 353, 373, 423, 473 K. **Inset:** Comparison of the $\nu(\text{O-H})$ bands of free OH groups after different pretreatments: (α) in helium at 300 K before H₂O adsorption; (β) and (λ) at the adsorption equilibrium using 3% H₂O/He at T_a = 300 K and T_a = 530 K, respectively.

The adsorption of 1% NH₃/He at 300 K led to the appearance of three bands due to NH_{3ads} species and ascribed as follows: (a) 1638 cm⁻¹ (spectrum a, Fig. 1A) corresponds to the $\delta_{as}(\text{NH}_3)$ vibration^{19,48,49} (the $\delta_s(\text{NH}_3)$ symmetric deformation which gives one IR band below

1300 cm^{-1} was not detected because of the strong IR absorption of the solid) and (b) 3403 and 3320 cm^{-1} (see Fig. S1) were due to the asymmetric and symmetric $\nu(\text{NH}_3)$ stretching vibrations, respectively.^{1,20} The band observed at 3260 cm^{-1} (Fig. S1) was attributed to the overtone of the $\delta_{\text{as}}(\text{NH}_3)$ band.⁴⁹ NH_3 adsorption led to a strong decrease in the $\nu(\text{O-H})$ band at 3742 cm^{-1} (inset Fig. 1A, spectrum λ) and the detection of a broad band in the range 3500-2600 cm^{-1} indicating the formation of $\text{Si-OH}\dots\text{NH}_{3\text{ads}}$ hydrogen bonds.^{1,20} Considering that this band is composed of two components (free and very weakly interacting SiOH species), a shift should be observed in parallel to its strong decrease if only one species interacted with NH_3 . Therefore, we assume that both species are involved in equivalent proportions in the formation of $\text{Si-OH}\dots\text{NH}_{3\text{ads}}$ hydrogen bonds. For the sake of clarity, the term ‘free OH groups’ corresponds in the following either to free OH groups and to very weakly interacting silanols.

The FTIR spectrum at 300 K is very similar to that observed by Tsyganenko et al.¹⁹ on SiO_2 Aerosil after a pretreatment at 873 K in vacuum ($<10^{-4}$ Torr) particularly considering the position of the $\delta_{\text{as}}(\text{NH}_3)$ band at 1638 cm^{-1} and the absence of band at ≈ 1450 cm^{-1} observed in some studies and ascribed to NH_4^+ (see below the impact of H_2O on NH_3 adsorption). Moreover, Bonelli et al.⁵⁰ studying the adsorption of NH_3 on SiO_2 Grace and 1% $\text{TiO}_2/\text{SiO}_2$ focused on the significant wavenumber difference in the δ_{as} band of $\text{NH}_{3\text{ads}}$ species adsorbed either on OH groups via H-bond: 1636 cm^{-1} (consistent with Fig. 1A) or on Ti^{4+} Lewis acid sites: 1606 cm^{-1} . Spectra b-e in Fig. 1A show that increasing the adsorption temperature T_a in the presence of 1% NH_3/He led to a progressive decrease in the absorbance of the $\delta_{\text{as}}(\text{NH}_3)$ band. It was associated with a shift to lower wavenumber (1624 cm^{-1} at 423 K) in parallel to an increase in the $\nu(\text{O-H})$ band at 3742 cm^{-1} (see Fig. S2 and note a new time the absence of shift with T_a increase and hence the coverage decrease). For $T_a > 423$ K: (a) the $\delta_{\text{as}}(\text{NH}_3)$ band was not detected (Fig. 1A) indicating that weakly adsorbed NH_3 species were present below and (b) the intensity of the $\nu(\text{O-H})$ band was identical to that recorded in helium after the pretreatment

procedure (Fig. S2) confirming that the adsorption equilibrium coverage of the $\text{NH}_{3\text{ads}}$ species was ≈ 0 for $P_{\text{NH}_3} = 1$ kPa at $T_a > 423$ K.

Figure 1B shows the IR bands observed after adsorption of 3% $\text{H}_2\text{O}/\text{He}$ at 300 K on the pretreated SiO_2 solid: there is a strong band at 1628 cm^{-1} due to the $\delta(\text{H}_2\text{O})$ bending band of molecularly adsorbed $\text{H}_2\text{O}_{\text{ads}}$ species associated with a broad band in the $3600\text{--}2800\text{ cm}^{-1}$ ascribed to $\nu(\text{O-H})$ of interacting SiOH groups and adsorbed H_2O molecules in H-bonding with other surface species.^{13,43} In particular, spectra α and β in the inset of Fig. 1B show a strong decrease in the $\nu(\text{O-H})$ band without any shift after H_2O adsorption at 300 K associated with a very broad IR in the range $3700\text{--}2800\text{ cm}^{-1}$. Note that at the adsorption equilibrium for $P_{\text{H}_2\text{O}} = 3$ kPa, the observation of remaining free OH groups implies that the adsorption equilibrium coverage of the $\text{H}_2\text{O}_{\text{ads}}$ species was lower than 1. Figure 1B shows that an increase in T_a in the presence of 3% $\text{H}_2\text{O}/\text{He}$ led to a progressive decrease in the $\delta(\text{H}_2\text{O})$ band associated with a slight shift to lower wavenumbers (1625 cm^{-1} for $T_a > 373$ K). The band was not detected for $T_a \geq 473$ K indicating that the adsorption equilibrium of the $\text{H}_2\text{O}_{\text{ads}}$ species was ≈ 0 for $P_{\text{H}_2\text{O}} = 3$ kPa. Spectrum λ in the inset of Fig. 1B shows that the intensity of the $\nu(\text{OH})$ band at $T_a = 503$ K after the removal the $\text{H}_2\text{O}_{\text{ads}}$ species was not identical to that after the pretreatment procedure (spectrum α). This seems due to the fact that in the presence of H_2O , dissociative adsorption/hydrolysis on small amount of SiOSi siloxane sites, leads to the formation of new OH groups which could interact with OH groups present after the pretreatment procedure. The formation of new OH groups during the adsorption of H_2O at 300 K on SiO_2 has been considered in early works^{2,13,43,44,51} to explain the superposition of a slow process (with an activation energy) to the fast-molecular adsorption of H_2O . It must be noted that the $\delta_{\text{as}}(\text{NH}_3)$ and $\delta(\text{H}_2\text{O})$ bands (Fig. 1A and 1B, respectively) were detected in very close wavenumber ranges. This constitutes a difficulty in the identification of adsorbed species formed during NH_3 -

H₂O coadsorption. However, the absorbance of the $\delta(\text{H}_2\text{O})$ band for $P_{\text{H}_2\text{O}} = 3$ kPa was strongly higher (factor ≈ 10) than the $\delta_{\text{as}}(\text{NH}_3)$ one for $P_{\text{NH}_3} = 1$ kPa.

Heat of adsorption of H₂O and NH₃ on SiO₂ using the AEIR method

The AEIR method imposes determining of A_M the area of the IR band of adsorbed species at full coverage (Eq. S1). For strongly adsorbed species, this can be obtained at the lowest adsorption temperature available with the setup (RT in the present study) by showing that the band is not modified either by increasing T_a in isobaric conditions or P_a in isothermal conditions. This experimental procedure is rarely applicable for “weakly” adsorbed species such as $\text{NH}_{3\text{ads}}$ and $\text{H}_2\text{O}_{\text{ads}}$ on SiO_2 . Thus, A_M used in Eq. S1 of the S.I. must be estimated by studying at 300 K the increase in the A intensity with the adsorption pressure P_a providing $A = f(P_a)$.³¹ Then, these data can be exploited via the Langmuir model according to Eq. S2 which shows that $1/A = f(1/P_a)$ must be a straight-line giving A_M for $1/P_a = 0$. For instance, the circle symbols in the insert of Fig. 2 provided $1/A_{\text{H}_2\text{Oads}} = f(P_{\text{H}_2\text{O}})$ with $A_{\text{H}_2\text{Oads}}$ the area of the $\delta(\text{H}_2\text{O})$ band at 1628 cm^{-1} at 300 K and then A_M for this IR band. The coverage of $\text{H}_2\text{O}_{\text{ads}}$ species $\theta_{\text{H}_2\text{O}}(T_a, 3\text{ kPa})$ at different adsorption temperature was then calculated (black circle symbols in Fig. 2) from the data in Figure 1B using Eq. S1 (for instance, $\theta_{\text{H}_2\text{O}}(300\text{ K}, P_{\text{H}_2\text{O}} = 3\text{ kPa})$ is equal to 0.83). Note that the AEIR method is based on a linear relationship between the amounts of an adsorbed species on the surface and the absorbance of its IR bands. It has been shown that this is true for different adsorbed species such as linear CO species⁵² on supported metal particles and $\text{NH}_{3\text{ads}}/\text{NH}_4^+$ species on different TiO_2 based solids.³⁵⁻³⁷ For H_2O on SiO_2 , this linear relationship has been clearly checked by Gallas et al.⁴⁵ on five types of SiO_2 solid with BET area in the range $220\text{-}765\text{ m}^2/\text{g}$ in particular SiO_2 Grace and the slope of the straight line was independent of the SiO_2 solid. Similar calculations lead to the evolution of the coverage of the $\text{NH}_{3\text{ads}}$ species from the data plotted in Fig. 1A as shown by the red square symbols in Fig. 2 and for instance, $\theta_{\text{NH}_3}(300\text{ K}, P_{\text{NH}_3} = 1\text{ kPa}) = 0.87$.

Curves a and b which overlap the black circle and red square symbols, respectively were obtained using the Langmuir adsorption model (Eq. S2 and Eq. S4 of the S.I.) for $P_{\text{H}_2\text{O}} = 3 \text{ kPa}$ and $P_{\text{NH}_3} = 1 \text{ kPa}$ and the following heats of adsorption: $E_{\text{L}(\text{H}_2\text{O}_{\text{ads}})} = 49 \text{ kJ/mol}$ and $E_{\text{L}(\text{NH}_3_{\text{ads}})} = 53 \text{ kJ/mol}$. Note that heats of adsorption different by $\pm 1 \text{ kJ/mol}$ lead to theoretical curves significantly different from the experimental data (see Fig. S3).

Figure 2. Coverage of molecularly adsorbed NH_3_{ads} and $\text{H}_2\text{O}_{\text{ads}}$ species on $\text{SiO}_2\text{-G}$ using the AEIR method and $\text{NH}_3\text{-H}_2\text{O}$ coadsorption. Black circle and red square symbols: experimental coverages of the $\text{H}_2\text{O}_{\text{ads}}$ and NH_3_{ads} species, respectively using Fig. 1B and 1A, respectively; blue square symbols: experimental coverage of the NH_3_{ads} species using the $\nu(\text{O-H})$ band of free OH groups; curves a and b: theoretical coverages of the $\text{H}_2\text{O}_{\text{ads}}$ and NH_3_{ads} species, respectively using the Langmuir adsorption model; curves c and d: theoretical coverages of $\text{H}_2\text{O}_{\text{ads}}$ and NH_3_{ads} species for 1% $\text{NH}_3/3\%$ $\text{H}_2\text{O}/\text{He}$ considering the competitive Langmuir model. **Inset:** Determining of A_{M} for the $\delta(\text{H}_2\text{O})$ band using the Langmuir model at 300 K for $P_{\text{a}} = 500 \text{ Pa}$, 1000 Pa and 2000 Pa .

The experimental data were also fitted (see Fig. S4) using the Temkin model (Eq. S3 and Eq. S4 of the S.I.) with similar heats of adsorption at high and low coverage such as (a) $E_0(\text{H}_2\text{O}_{\text{ads}}) = 49.1 \text{ kJ/mol}$ and $E_1(\text{H}_2\text{O}_{\text{ads}}) = 49.0 \text{ kJ/mol}$ and (b) $E_0(\text{NH}_3_{\text{ads}}) = 53.1 \text{ kJ/mol}$ and $E_1(\text{NH}_3_{\text{ads}}) = 53.0 \text{ kJ/mol}$. Note that the heats of adsorption are necessarily higher than the latent heats of liquefaction of H_2O and NH_3 at 300 K: 44.0 kJ/mol^{12} and 21.7 kJ/mol^{53} respectively.

In an early study, Hertl and Hair¹⁶ have determined the isosteric heat of adsorption of NH_3 on SiO_2 Car-O-Sil in a short coverage range (0.5-0.6) (due to experimental difficulties for the other coverages) by using the change in the intensity of the $\nu(\text{O-H})$ band of free OH groups due the formation of H-bonded NH_3_{ads} . According to a classical approach at an adsorption equilibrium, the OH adsorption sites are either free (with coverage θ_{OH}) or H-bonded to NH_3_{ads} (coverage $\theta_{\text{NH}_3_{\text{ads}}}$), leading to $\theta_{\text{OH}}(T_a) + \theta_{\text{NH}_3_{\text{ads}}}(T_a) = 1$. This shows that the measurement of the fraction of the free OH groups during NH_3 adsorption provides the coverage of the NH_3_{ads} species. This approach¹⁶ has been then used by different groups to determine the coverage of the OH groups at the adsorption equilibrium of molecules such ammonia¹ and acetone.⁵⁴ For comparison with the AEIR method, it has been used considering the evolution of the absorbance of the $\nu(\text{O-H})$ band at 3742 cm^{-1} (inset Fig. 1A) during the heating in isobaric conditions (Fig. 1A). For instance, considering the inset of Fig. 1A (see also Fig. S1) the ratio of the intensity of the bands before (spectrum β) and after (spectrum λ) adsorption equilibrium leads to: $\theta_{\text{OH}}(300 \text{ K}) = 0.17$ and hence $\theta_{\text{NH}_3_{\text{ads}}}(300 \text{ K}) = 0.83$ which is consistent with the value determined from the AEIR method: 0.87. In Fig. 2, the overlap of the experimental data obtained using the absorbances of the $\nu(\text{O-H})$ band of free OH groups (blue square symbols) and the NH_3_{ads} adsorbed species (red square symbols) also confirms clearly that the FTIR data are relevant of H-bonded NH_3_{ads} species on free OH groups (and very weakly interacting SiOH, see above) of SiO_2 . Note that this consistency implies that only these species are involved in the adsorption process and not the interacting SiOH ones leading to the broad band in the range

3700-3200 cm^{-1} . However, as the $\nu(\text{O-H})$ band of the free OH groups is partially overlapped with the broad band of all the H-bonds, it imposed a decomposition before measuring the band intensity. This overlap explains that $\theta_{\text{NH}_3\text{ads}} = f(T_a)$ in isobar condition cannot be determined with accuracy in the full range of T_a (300-423 K, see Fig. 2) according to this procedure. Indeed, the simultaneous increase in the $\nu(\text{O-H})$ band of free OH groups and decrease in the band of H-bonds lead to a complex situation for the decomposition of the two spectral components. This was probably one of the difficulties encountered by Hertl and Hair.¹⁶ However, due to the low heats of adsorption of $\text{NH}_{3\text{ads}}$ species a limited increase in T_a for $P_{\text{NH}_3} = 1$ kPa such as $T_a = 313$ K leads to a significant increase in θ_{OH} value whereas the decomposition of the IR bands is still possible (see Fig. S1). In this case, $\theta_{\text{OH}}(313 \text{ K}) = 0.37$ and hence $\theta_{\text{NH}_3}(313 \text{ K}) = 0.63$ which is a value consistent with the AEIR method (see the blue square symbols in Fig. 2). A third experimental data is reported in Fig. 2 by a blue square symbol obtained at $T_a = 423$ K, leading to $\theta_{\text{OH}} = 1$ (at this temperature the $\nu(\text{O-H})$ bands of the free OH groups are identical before and after adsorption of NH_3) and $\theta_{\text{NH}_3} = 0$ for 1% NH_3/He . Note that using the intensity of the $\nu(\text{O-H})$ bands of SiO_2 Aerosil, Armandi et al.¹ were able to follow the coverage of the free OH groups in isothermal conditions ($T_a = 303$ K) for P_{NH_3} pressure in the 0-40 mbar range (see Fig. 4 in Ref. 1). This is mainly due to the higher pretreatment temperature (1073 K) than in the present study (723 K) which leads to a sharper profile of the $\nu(\text{O-H})$ band of free OH groups (the shoulder at low wavenumbers in inset Fig. 1A is not observed) preventing a decomposition procedure for the quantification of the coverage of the OH groups. Note also that on SiO_2 Aerosil solid, the authors¹ concluded that the experimental isotherm is consistent with the Langmuir adsorption model which agrees with the present conclusion from curve b in Fig. 2 using isobaric conditions. Moreover, the authors determined the experimental adsorption coefficient at 303 K of the Langmuir adsorption model: $K_L = 0.117 \pm 0.005 \text{ mbar}^{-1}$. Considering the expression of the adsorption coefficient used in the AEIR method (Eq. S4), this value leads

to a heat of adsorption of 49.6 kJ/mol for the $\text{NH}_{3\text{ads}}$ species consistent with the value determined in the present study: 53 kJ/mol.

The approach of Hertl and Hair¹⁶ cannot be applied for the adsorption of H_2O because surface processes other than the molecular adsorption of H_2O on the OH groups were operant (see Part 3.1).

Comparison to literature data of the heat of adsorption of $\text{NH}_{3\text{ads}}$ on $\text{SiO}_2\text{-G}$

The heat of adsorption of $\text{NH}_{3\text{ads}}$ species adsorbed via H-bond with the free OH groups of the SiO_2 solid: 53 kJ/mol was compared to experimental literature data. Hertl and Hair¹⁶ seem to be the first ones to provide a value of the isosteric heat of adsorption in the coverage range 0.5-0.6: 37.2 ± 0.8 kJ/mol from the Clausius-Clapeyron equation by using the change in the intensity of the $\nu(\text{O-H})$ band of free OH groups on Cab-O-Sil SiO_2 (150 m^2/g). However, the isosteric method is highly sensitive to experimental uncertainties.³¹ In parallel to the FTIR study of the adsorption of NH_3 on SiO_2 Aerosil, Armandi et al.¹ measured the differential heats of adsorption of NH_3 using microcalorimetry. They concluded that in their experimental conditions (in particular the high pretreatment temperature 1073 K), a second adsorbed NH_3 species (named unspecific adsorption) having no significant impact on the FTIR data contributes to their microcalorimetric measurements. Using an adsorption model considering two types of adsorption sites they concluded that the heats of adsorption of $\text{NH}_{3\text{ads}}$ species on the free OH group is 58.4 kJ/mol which is consistent with the value obtained from the AEIR method (53 kJ/mol) while the one of the second adsorbed species is 26.9 kJ/mol. Cardona-Martinez and Dumesic⁵³ have measured the differential heat of adsorption of NH_3 on SiO_2 and $\text{SiO}_2\text{-Al}_2\text{O}_3$ at 423 K. A value of 70 kJ/mol was determined for SiO_2 which was consistent with literature data obtained at 300 K (see more details in Ref. 53). This value is significantly different from that obtained with the AEIR method. However, it must be noted that the adsorption temperature selected i.e. 423 K,⁵³ leads to a very low coverages of $\text{NH}_{3\text{ads}}$ species

on free OH groups (see Fig. 2) and probably their measurements concerned mainly a different adsorbed species (see below the TPAE data). Interestingly, Gervasini et al.⁵⁵ have determined using microcalorimetry that the heat of NH₃ adsorption on SiO₂-G pretreated at 773 K in vacuum is 83 kJ/mol at low coverages due to the presence of very few acidic sites. Bolis et al.²⁰ have measured the heat of adsorption of NH₃ at room temperature on different silicates and the amorphous SiO₂ aerosil 300 using microcalorimetry. On this solid dehydrated at 973 K they determined values in the range 46-62 kJ/mol at high and low coverages: the average (54 kJ/mol) is consistent with the value from the AEIR value. Fubini et al.¹⁷ have measured using microcalorimetry the heat of adsorption of NH₃ on SiO₂ cristobalite (6.2 m²/g) at 300 K for pretreatment temperature in vacuum in the range 423-773 K: they determined a value of 53 ± 1 kJ/mol which is consistent with the present study. At higher pretreatment temperatures i.e. 1073 K and 1573 K, the heat of adsorption of NH₃ decreased to 44 kJ/mol and 20 kJ/mol, respectively. Moreover, similarly to the present study, Helminen et al.⁵⁶ have observed on Fluka silica gel 60 that NH₃ adsorption isotherms are consistent with the Langmuir model leading to an isosteric heat of adsorption of 53 kJ/mol identical to that determined from the AEIR method.

Finally, it can be concluded that the heat of adsorption of the H-bonded NH₃ species on free OH groups of SiO₂-G obtained by the AEIR method is consistent with some microcalorimetric literature data on others SiO₂ solids dehydrated/dehydroxylated at similar temperatures (see Table 1) whereas the experimental procedure is significantly simplified which is an important outcome of this work.

Table 1: Comparison of the heats of adsorption of the molecularly adsorbed NH₃ and H₂O species on SiO₂ determined with the AEIR method to microcalorimetric literature data.*

Reference	Heat of adsorption (kJ/mol)
This study (AEIR method)**	53
1	58.4 (on free OH) 26.9 (on second species)

NH _{3ads}	16	37.2 ± 0.8
	17	53 ± 1
	20	46-62
	53	70 (low coverage)
	55	83 (low coverage)
Reference		Heat of adsorption (kJ/mol)
H ₂ O _{ads}	This study (AEIR method)	49
	13	90 (low coverage)
		44 (high coverage)
	20	53±1
	57	49

*: the comparison must consider the differences in the type of SiO₂ solid and its dehydration temperature (see more details in the cited references).

**: the TPAE method indicates that a second minor species contributes to the NH₃ adsorption (≈ 13%) with heats of adsorption varying linearly with the coverage from 72 to 52 kJ/mol at low and high coverages.

Comparison of the heat of adsorption of the H₂O species on SiO₂-G to literature data.

The heat of adsorption on the H-bonded H₂O_{ads} species with the free OH groups of SiO₂: 49 kJ/mol was compared to experimental literature data. The difficulty in the comparison with microcalorimetry measurements is that dissociative and molecularly adsorption of H₂O may contribute to the measurement.^{2,13,43,44,51} For instance, on Aerosil 380 and 50 dehydrated at 423 K, Bolis et al.¹³ have observed that the heat of adsorption of H₂O decreased from ≈ 90 kJ/mol at low coverages to value slightly either higher or lower than 44 kJ/mol at high coverages. The data at high coverages are consistent with the one of our study whereas the data at low coverage are mainly due to dissociative adsorption of H₂O. In a second study,²⁰ the same group has studied the heat of adsorption of H₂O at 300 K for a H₂O partial pressure of 5 torr: 53±1 kJ/mol on cristobalite pretreated in vacuum in the range 423-773 K. This value is consistent with that

obtained from the AEIR method. Moreover, the heats of adsorption for the $\text{H}_2\text{O}_{\text{ads}}$ and NH_3_{ads} determined by this group were similar which is in line with the conclusions of the AEIR method. Finally, Pedram and Hines⁵⁷ have studied using a gravimetric method the H_2O adsorption in the temperature range 300-326 K on a Mobil silica gel ($650 \text{ m}^2/\text{g}$). They showed that the isosteric heats of adsorption is independent on the coverage and reported a value of ca 49 kJ/mol which is the value determined by the AEIR method using the Langmuir model. The comparison with microcalorimetry measurements discussed in this section is summarized in Table 1.

Theoretical impact of the NH_3 - H_2O coadsorption on the coverage of the adsorbed species

Assuming that the NH_3_{ads} and $\text{H}_2\text{O}_{\text{ads}}$ are adsorbed on the same SiOH groups then considering the heats of adsorption of the $\text{H}_2\text{O}_{\text{ads}}$ and NH_3_{ads} species, the curves c and d plotted in Fig. 2 show their theoretical coverage evolutions, respectively with the coadsorption temperature for $P_{\text{NH}_3} = 1 \text{ kPa}$ and $P_{\text{H}_2\text{O}} = 3 \text{ kPa}$. These curves are based on a Langmuir competitive adsorption model providing the evolutions of the coverages of two molecularly adsorbed species such as $A = \text{NH}_3_{\text{ads}}$ and $B = \text{H}_2\text{O}_{\text{ads}}$ on the same adsorption sites with an increase in the coadsorption temperature T_a for fixed (isobaric) P_A and P_B partial pressures (see Ref. 29 and references therein):

$$\theta_A(T_a, P_A, P_B) = \frac{K_A(T_a, P_A)}{1 + K_A(T_a, P_A) + K_B(T_a, P_B)} \quad \text{Eq. 1}$$

$$\theta_B(T_a, P_A, P_B) = \frac{K_B(T_a, P_B)}{1 + K_A(T_a, P_A) + K_B(T_a, P_B)} \quad \text{Eq. 2}$$

The calculations of the two coverages can be performed similarly to that described for the Temkin competitive adsorption model²⁹ using (a) Eq. S4 for the adsorption coefficients and (b) the heats of adsorption of the NH_3_{ads} and $\text{H}_2\text{O}_{\text{ads}}$ species determined from the AEIR method (Table 1). Comparison of curves c and d with curves a and b, respectively leads to the following comments: (a) at the co-adsorption equilibrium at 300 K, the two species can be present on the SiO_2 surface at coverages smaller than those of their adsorption equilibrium and (b) an increase

in T_a leads to a progressive decrease in the coverage of the two species which are at coverages 0 for $T_a > 450$ K. These theoretical data are compared to experimental FTIR and M.S. data during 1% NH_3 /3% H_2O /He coadsorption in the following.

Experimental studies of the NH_3 - H_2O coadsorption on SiO_2 using FTIR and M.S

Study using the FTIR cell

Figure 3A shows the evolution of the IR bands in the range 1800-1300 cm^{-1} on the pretreated SiO_2 -G solid during a switch $\text{He} \rightarrow 1\% \text{NH}_3/3\% \text{H}_2\text{O}/\text{He}$ at 300 K. An increase in time on stream t_a leads to an increase in the absorbance of the band at 1622 cm^{-1} which shifts progressively to 1628 cm^{-1} . For $t_a \geq 80$ s one band appears and increases at 1455 cm^{-1} whereas for $t_a > 121$ s the band at 1628 cm^{-1} decreases and shifts to 1634 cm^{-1} until a steady state at $t_a = 202$ s. For $t_a > 121$ s a small and broad shoulder is observed near 1670 cm^{-1} .

Figure 3. FTIR spectra recorded during the NH_3 - H_2O coadsorption on SiO_2 -G for 1% NH_3 /3% $\text{H}_2\text{O}/\text{He}$. **Part A:** Impact of the adsorption duration t_a at $T_a = 300$ K: (a)-(h) $t_a = 10, 23, 66, 78, 101, 121, 155, 202$ s. **Part B:** Impact of T_a the adsorption temperature at the adsorption equilibrium: (a)-(e) $T_a = 300, 313, 335, 373, 453$ in K.

The bands in Fig 3A can be ascribed as follows: (a) the one observed at 1622 cm^{-1} in spectrum a at $t_a = 10$ s can be ascribed to both $\delta_{\text{as}}(\text{NH}_3)$ and $\delta(\text{H}_2\text{O}_s)$ vibrations, (b) then the

increase in the band at 1628 cm^{-1} must be mainly due to the increase in the coverage of the $\text{H}_2\text{O}_{\text{ads}}$ species considering the difference in absorbance of the $\delta_{\text{as}}(\text{NH}_3)$ and $\delta(\text{H}_2\text{O})$ bands (see Figs 1A and 1B), (c) the band at $1455\text{--}1463\text{ cm}^{-1}$ was ascribed to the ν_2 asymmetric deformation of NH_4^+ species^{49,58} formed by either $\text{NH}_{3\text{ads}}$ or NH_3 with $\text{H}_2\text{O}_{\text{ads}}$ species (similarly to the dissolution of NH_3 in liquid H_2O)⁵⁹ and (c) the broad shoulder at 1670 cm^{-1} detected at the steady state was ascribed to the ν_4 symmetric deformation of NH_4^+ species.^{49,58} Observation of the latter band which is IR inactive for T_d symmetry (free NH_4^+) implies symmetry lowering due to interactions of NH_4^+ species with the SiO_2 surface. The decrease in the intensity of the $\delta(\text{H}_2\text{O})$ band is probably due to the impact of NH_3 dissolution.

Fig. 3B shows the evolution of the bands at the adsorption equilibrium during an increase in T_a for 1% NH_3 /3% $\text{H}_2\text{O}/\text{He}$. This led to a decrease in the $\nu_2(\text{NH}_4^+)$ band associated, at low temperatures, with an increase in the $\delta(\text{H}_2\text{O})$ one and then, the two bands decreased and were not detected anymore for $T_a > 473\text{ K}$. Figures 3A and 3B show that if FTIR spectroscopy revealed the formation of new NH_4^+ species on SiO_2 during the $\text{NH}_3\text{--H}_2\text{O}$ coadsorption, it did not provide clear data on the coverages of the $\text{NH}_{3\text{ads}}$ and $\text{H}_2\text{O}_{\text{ads}}$ species particularly considering that the absorbance of the $\delta(\text{H}_2\text{O})$ band is significantly higher than the $\delta_{\text{as}}(\text{NH}_3)$ one. This explains why experiments have been undertaken using a M.S system allowing the measurement of the amounts (in $\mu\text{mol/g}$) of adsorbed NH_3 and H_2O . These measurements are reported for $\text{SiO}_2\text{--A}$ leading to the same conclusion than those on $\text{SiO}_2\text{--G}$.

Study using the M.S system

The study of the NH_3 adsorption on the pretreated (723 K) solid in the absence of H_2O using M.S is a necessary step to characterize the impact of H_2O . Moreover, it provides supplementary data from those obtained by the FTIR method.

Figure 4A (part I) shows the evolution of the molar fractions of NH_3 and Ar during a switch $\text{He} \rightarrow 1\% \text{NH}_3/1\% \text{Ar/He}$ performed at 300 K. The total amount of NH_3 adsorbed at the steady state: $588 \mu\text{mol NH}_3/\text{g}$ corresponds to $1.6 \text{ NH}_3 \text{ molecules}/\text{nm}^2$ which is much lower than the theoretical amount needed to obtain a monolayer typically $10 \text{ molecules}/\text{nm}^2$. However, it is much higher than the OH surface density after pre-treatment ($0.8 \text{ OH}/\text{nm}^2$) and hence much higher than the free OH surface density. Therefore, we propose that after adsorption of the first NH_3 molecules on free OH species, the consecutive ones interact directly with the first ones. Furthermore, data in Fig. 2 indicates a coverage < 1 at 300 K for $P_{\text{NH}_3} = 1 \text{ kPa}$. Figure 4A (part II) shows that a switch $1\% \text{NH}_3/1\% \text{Ar/He} \rightarrow \text{He}$ at 300 K led to the progressive desorption of NH_3 until a low rate preventing the accurate measurement of the total amount of NH_3 desorbed from the surface.

Figure 4. Adsorption of NH_3 and coadsorption of $\text{NH}_3\text{-H}_2\text{O}$ at 300 K on $\text{SiO}_2\text{-A}$ using the M.S system. **Part A:** (I) adsorption of $1\% \text{NH}_3/1\% \text{Ar/He}$ and (II) isothermal desorption in helium. **Inset:** NH_3 production during TPD after (II). **Part B:** Coadsorption $1\% \text{NH}_3/2\% \text{H}_2\text{O}/1\% \text{Ar/He}$ and isothermal desorption on helium. **Inset:** NH_3 and H_2O productions during TPD after II.

Therefore, the desorption temperature was increased to facilitate the measurements as shown in the inset of Fig. 4A. The amounts of NH_3 desorbed in part II of Fig. 4A is of $495 \mu\text{mol}$ of NH_3/g while the consecutive TPD led to a production of $78 \mu\text{mol}$ of NH_3/g . The total amount

of NH_3 desorption $573 \mu\text{mol/g}$ is consistent with that adsorbed in part I of Fig. 4A considering the accuracy of measurements.

Figure 4B shows similar experiments at 300 K using 1% NH_3 /2% H_2O /1% Ar/He. The total amounts of NH_3 and H_2O adsorption in part I of Fig. 4B are of $630 \mu\text{mol NH}_3/\text{g}$ and $2618 \mu\text{mol of H}_2\text{O/g}$, respectively leading to a total amount of adsorbed species of ≈ 9.1 molecules/ nm^2 slightly lower than the monolayer (≈ 10 molecules/ nm^2). The amounts of NH_3 and H_2O desorbed at 300 K in part II are of $510 \mu\text{mol of NH}_3/\text{g}$ and $2247 \mu\text{mol H}_2\text{O/g}$, respectively. The inset of Fig. 4B shows that the remaining fraction of NH_3 ($125 \mu\text{mol of NH}_3/\text{g}$) desorbed during the TPD for $T_d \approx 500$ K. H_2O desorbed in two TPD peaks: the first is overlapped with that of NH_3 representing $134 \mu\text{mol of H}_2\text{O/g}$ and the second at $T_M \approx 600$ K is of $250 \mu\text{mol of H}_2\text{O/g}$. The total amounts of NH_3 ($635 \mu\text{mol/g}$) and H_2O ($2631 \mu\text{mol/g}$) are consistent with the amount adsorbed in part I of Fig. 4B. The data in Fig. 4A and 4B shows that the amount of NH_3 adsorbed at 300 K was increased by $49 \mu\text{mol/g}$ in the presence of H_2O whereas the calculations similar to those performed to obtain curves c and d in Fig. 2 indicate that the coverage of the $\text{NH}_{3\text{ads}}$ species decreased by $\approx 25\%$ after introduction of $P_{\text{H}_2\text{O}} = 2$ kPa with $P_{\text{NH}_3} = 1$ kPa. Two processes must contribute to this situation: (a) Figs. 3A-3B show that the adsorption of H_2O and NH_3 is associated with the formation of the NH_4^+ species and (b) the second H_2O TPD peak (inset Fig. 4B) indicates that dissociative adsorption/hydrolysis of SiOSi bridges is operant in the presence of H_2O leading to an increase in the OH groups which can be new adsorption sites for NH_3 .

To obtain more details on the NH_3 - H_2O coadsorption on SiO_2 , experiments similar to Figs. 1A and 3B have been performed using the M.S system.

Figure 5. Impact of the T_a adsorption temperature on the amount of NH_3 on the $\text{SiO}_2\text{-A}$ surface in the absence (Part A) and in the presence (part B) of H_2O using the TPAE procedure. **Part A:** Evolution of the NH_3 molar fraction during (I) an increase and (II) a decrease in T_a respectively using 1% NH_3 /1% Ar/He . **Part B:** Evolutions of the molar fraction of NH_3 and H_2O during an increase in the adsorption temperature using 1% NH_3 /3% H_2O /1% Ar/He . **Inset:** Comparison of the NH_3 productions in Fig. 5A and 5B during an increase in T_a .

For instance, after the adsorption equilibrium at 300 K using 1% NH_3 /1% Ar/He (same as Fig. 4A, part I), T_a was increased in the presence of NH_3 , according to the TPAE procedure.³² This led to a progressive decrease in the adsorption equilibrium of the $\text{NH}_{3\text{ads}}$ species associated with an increase in the P_{NH_3} at the outlet of the reactor as shows Fig 5A, Part I. It can be observed that the NH_3 production was ended at $T_a \approx 450$ K which is consistent with the FTIR data in Fig. 1A. The total amount of NH_3 desorbed from the surface was $554 \mu\text{mol/g}$, which is consistent with the amount adsorbed in Fig. 4A. Part II in Figure 5A shows that a decrease in T_a to 300 K led to the readsorption of NH_3 in an amount equal to that removed from the surface in part I. This confirms the reversibility of the adsorbed NH_3 species and the absence of modification of the SiO_2 surface during the experiments. The data in Fig. 5A can be used according to the TPAE method³² to measure the average coverage of the adsorbed NH_3 species and then, their heats of adsorption.

Heat of adsorption of the $\text{NH}_{3\text{ads}}$ species on $\text{SiO}_2\text{-A}$ using the TPAE procedure

Using Eq. S6 of the S.I., the data reported in part I of Fig. 5A (represented as curve a in Fig. 6 providing the difference between the outlet and inlet molar fractions of NH_3 during an increase in T_a) provide the evolution of the average coverage of the adsorbed NH_3 species with T_a in “quasi” isobaric conditions ($P_{\text{NH}_3} \approx 1 \text{ kPa}$)³² as shown by the blue square symbols in Fig. 6. The coverage at 300 K was determined from the FTIR spectra. Curve b which overlaps the experimental data in a large range of coverage has been obtained using the Langmuir adsorption model (Eq. S2) with the same heat of adsorption as the one used in Fig. 2 for $\text{SiO}_2\text{-G}$: $E_L = 53 \text{ kJ/mol}$ showing that FTIR and M.S. measurements lead to similar values on the two SiO_2 solids. However, at high temperatures the experimental data are slightly higher than curve b. This can be due to the accuracy of the MS measurements during the TPAE procedure when the molar fraction at the outlet of the reactor becomes close to the inlet molar fraction (as shown by curve a in Fig. 6).

Figure 6. Study of NH_3 adsorption using the TPAE procedure with 1% NH_3 /1% Ar/He . (a): evolution with T_a of the relative molar fraction ($\text{NH}_3(T_a)_{\text{out}} - \text{NH}_3(T_a)_{\text{in}}$) from Fig. 5A part I; blue square symbols: evolution of the average adsorption equilibrium coverage of the $\text{NH}_{3\text{ads}}$

species from curve a; (b) theoretical evolution of the coverage according to the Langmuir model considering the presence of one adsorbed $\text{NH}_{3\text{ads}}$ species with an heat of adsorption of $E_L = 53$ kJ/mol; (c) theoretical evolution of the coverage considering the presence of two adsorbed $\text{NH}_{3\text{ads1}}$ and $\text{NH}_{3\text{ads2}}$ species which obey to the Langmuir ($E_L = 53$ kJ/mol) and Temkin ($E_0 = 72$ kJ/mol, $E_1 = 52$ kJ/mol) adsorption model, respectively with $x_{\text{NH}_{3\text{ads1}}} \approx 0.87$ and $x_{\text{NH}_{3\text{ads2}}} \approx 0.13$ for their respective contribution to the average coverage at 300 K.

However, it can be suggested that there is a minor amount of a second adsorbed $\text{NH}_{3\text{ads}}$ species contributing in Fig. 6 to the TPAE data at high temperatures whereas it does not contribute to the FTIR data. For instance, curve c in Fig. 6 which overlaps with the experimental data is obtained from Eq. S5 considering that two $\text{NH}_{3\text{ads1}}$ and $\text{NH}_{3\text{ads2}}$ adsorbed species contribute to the average coverage of the NH_3 species with the following parameters: (a) $\text{NH}_{3\text{ads1}}$ obeys to the Langmuir adsorption model with a heat of adsorption of $E_L = 53$ kJ/mol, (b) $\text{NH}_{3\text{ads2}}$ obeys to the Temkin adsorption model with heats of adsorption of $E_0 = 72$ kJ/mol and $E_1 = 52$ kJ/mol and (c) their contribution to the total amount of NH_3 adsorbed at saturation of the sites at 300 K are $x_{\text{NH}_{3\text{ads1}}} \approx 0.87$ and $x_{\text{NH}_{3\text{ads2}}} \approx 0.13$. It can be noted that only the $\text{NH}_{3\text{ads2}}$ species contributes significantly to the average coverage at $T_a > 410$ K (Figure 6). This allows a comparison of its heats of adsorption with the microcalorimetric measurement performed at 423 K in Ref. 53: 70 kJ/mol. As mentioned in the introduction, the presence of adsorption sites different from free silanols has been considered in different studies: partially strained patches at the surface of dehydrated silica dehydrated¹ and terminal group of arrays of interacting SiOH for partially dehydrated silica.^{17,20,21}

Figure 5B shows similar TPAE experiments using a 1% NH_3 /3% H_2O /1% Ar/He gas mixture. It can be observed that the coadsorption equilibrium coverage of the $\text{H}_2\text{O}_{\text{ads}}$ and $\text{NH}_{3\text{ads}}$ species decreases simultaneously until 0 at 470 K which is consistent with the FTIR data in Fig. 3B. Note that the absence of a second H_2O peak similar to the TPD procedure (inset of Fig. 4B)

indicates that, in the presence of $P_{\text{H}_2\text{O}} = 3$ kPa and in the range of temperature of Fig. 5B, the coverage of the OH species formed during H_2O adsorption is not significantly modified (high heats of adsorption). The inset of Fig. 5A which compares the NH_3 molar fractions during the TPAE procedures with 1% NH_3 /1% Ar/He (curve a) and 1% NH_3 /3% H_2O /1% Ar/He (curve b) shows that the presence of H_2O has a limited impact in the temperature range leading to the total desorption of the NH_3 species. However, two peaks are present in curve b consistent with the presence of $\text{NH}_{3\text{ads}}$ and NH_4^+ species on the surface (Fig. 3B). The total amounts of desorbed NH_3 and H_2O in Fig. 5B are 543 $\mu\text{mol/g}$ and 4990 $\mu\text{mol/g}$, respectively. The amount of H_2O exceeds slightly that of the monolayer: 14 molecules/ nm^2 .

Average Coverage of the adsorbed NH_3 species during TPAE using 1% NH_3 /3% H_2O /1% Ar/He

The TPAE data in Fig. 5B can be used to determine the evolution of the average coverage of the adsorbed NH_3 species in isobaric conditions ($P_{\text{NH}_3} = 1$ kPa) using 1% NH_3 /3% H_2O /1% Ar/He according to Eq. S6 as shown by the blue square symbols in Fig. 7. Considering the limited difference in the amount of NH_3 adsorbed in the presence and in the absence of H_2O , we have assumed a similar average coverage of the adsorbed NH_3 species at 300 K for the two experimental conditions. Curve b in Fig. 7 has been obtained using the Langmuir adsorption model with $E_L = 53$ kJ/mol and $P_{\text{NH}_3} = 1$ kPa. As compared to Fig. 6, it can be observed that curve a overlaps with the experimental data in a shorter range of adsorption temperature. This comes mainly from a decrease in the coverage of H-bonded $\text{NH}_{3\text{ads}}$ species due to the competitive adsorption with H-bonded $\text{H}_2\text{O}_{\text{ads}}$ species (compare curve b and d in Fig. 2). This is clearly shown considering curve c in Fig. 7 which overlaps with the experimental data considering two $\text{NH}_{3\text{ads}1}$ and $\text{NH}_{3\text{ads}2}$ species with the following parameters: (a) $\text{NH}_{3\text{ads}1}$ obeys to the Langmuir adsorption model with a heat of adsorption of $E_L = 52$ kJ/mol, (b) $\text{NH}_{3\text{ads}2}$ species obeys to the Temkin adsorption model with heats of adsorption $E_0 = 74$ kJ/mol and $E_1 =$

53 kJ/mol and (c) their contribution to the total amount of NH_3 adsorbed at saturation of the sites at 300 K are $x_{\text{NH}_3\text{ads1}} \approx 0.6$ and $x_{\text{NH}_3\text{ads2}} \approx 0.4$.

Figure 7. Study of NH_3 adsorption using the TPAE procedure with 1% NH_3 /3% H_2O /1% Ar/He . (a): evolution with T_a of the relative molar fraction ($\text{NH}_3(T_a)_{\text{out}} - \text{NH}_3(T_a)_{\text{in}}$) from Fig. 5B; blue square symbols: evolution of the average coadsorption equilibrium coverage of the NH_3ads species from curve a; (b) theoretical evolution of the coverage according to the Langmuir adsorption model with a heat of adsorption $E_L=53$ kJ/mol; (c) theoretical evolution of the coverage considering the presence of two adsorbed $\text{NH}_3\text{ads1}$ and $\text{NH}_3\text{ads2}$ species which obey to the Langmuir ($E_L=52$ kJ/mol) and Temkin ($E_0=74$ kJ/mol, $E_1=53$ kJ/mol) adsorption model, respectively with $x_{\text{NH}_3\text{ads1}} \approx 0.6$ and $x_{\text{NH}_3\text{ads2}} \approx 0.4$ for their respective contribution to the average coverage at 300 K.

Note that the decrease in the contribution of the H-bonded NH_3 species (from 0.87 to ca 0.6 in the absence and presence of H_2O , respectively) without major change in its heats of adsorption is consistent with the outcome of the Temkin competitive model (Fig. 2). The second adsorbed species contributing to the average coverage in curve c is probably linked to the NH_4^+ species. However, this cannot be clearly justified via quantitative data because their amounts on the surface result from several surface processes.

CONCLUSION

FTIR and S.M data lead to the conclusion that the SiO₂ supports may adsorb NH₃ and H₂O mainly via H-bonds with the free OH groups. The two NH_{3ads} and H₂O_{ads} species obey to the Langmuir model and they have slightly different heats of adsorption: ≈ 53 kJ/mol and ≈ 49 kJ/mol, respectively explaining that their coverages are decreased during NH₃-H₂O coadsorption. Minor amounts of others adsorbed NH₃ species more strongly bonded to the surface and not detected via FTIR spectroscopy may contribute to the NH₃ adsorption at high temperatures. Moreover, the molecular adsorption of H₂O is associated with hydrolysis of SiOSi bridged formed during the pretreatment at high temperatures leading to new OH groups. During NH₃-H₂O coadsorption, NH₄⁺ species are formed involving H₂O_{ads} species. The present study also highlights that adsorbed NH₃ species on SiO₂ cannot contribute to the NH₃ adsorption on metal oxides supported SiO₂ catalysts in the absence and in the presence of H₂O for adsorption temperatures $T_a > 450$ K.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX.

Heats of adsorption of adsorbed species using the AEIR Method, Heats of adsorption of adsorbed species using the TPAE Method, IR bands in the 3800-2800 cm⁻¹ range on SiO₂-Grace before and after adsorption of 1% NH₃/He, IR bands of the OH groups on SiO₂-G during the adsorption of 1% NH₃/He for T_a in the range 300-423 K, Impact of the heats of adsorption on the fitting of the experimental data of the AEIR method, Application of the Temkin model as case limit of the Langmuir model.

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FIGURES CAPTIONS

Figure 1. FTIR spectra recorded during adsorption of NH_3 (part A) and H_2O (part B) on $\text{SiO}_2\text{-G}$. **Part A:** Impact of the adsorption temperature T_a on the intensity of the $\delta_{\text{as}}(\text{NH}_3)$ band of $\text{NH}_{3\text{ads}}$ species for 1% NH_3/He : (a)-(e) $T_a = 300, 323, 343, 423, 473$ K. **Inset:** Comparison of the $\nu(\text{O-H})$ bands of free OH groups after different pretreatments: (α) in helium at 723 K; (β) at 300 K after cooling from 723 K; (λ) at the adsorption equilibrium at 300 K using 1% NH_3/He . **Part B:** Impact of the adsorption temperature T_a on the intensity of the $\delta(\text{H}_2\text{O})$ band of $\text{H}_2\text{O}_{\text{ads}}$ species for 3% $\text{H}_2\text{O}/\text{He}$: (a)-(g) $T_a = 300, 323, 353, 373, 423, 473$ K. **Inset:** Comparison of the $\nu(\text{O-H})$ bands of free OH groups after different pretreatments: (α) in helium at 300 K before H_2O adsorption; (β) and (λ) at the adsorption equilibrium using 3% $\text{H}_2\text{O}/\text{He}$ at $T_a = 300$ K and $T_a = 530$ K, respectively.

Figure 2. Coverage of molecularly adsorbed $\text{NH}_{3\text{ads}}$ and $\text{H}_2\text{O}_{\text{ads}}$ species on $\text{SiO}_2\text{-G}$ using the AEIR method and $\text{NH}_3\text{-H}_2\text{O}$ coadsorption. Black circle and red square symbols: experimental coverages of the $\text{H}_2\text{O}_{\text{ads}}$ and $\text{NH}_{3\text{ads}}$ species, respectively using Fig. 1B and 1A, respectively; blue square symbols: experimental coverage of the $\text{NH}_{3\text{ads}}$ species using the $\nu(\text{O-H})$ band of free OH groups; curves a and b: theoretical coverages of the $\text{H}_2\text{O}_{\text{ads}}$ and $\text{NH}_{3\text{ads}}$ species, respectively using the Langmuir adsorption model; curves c and d: theoretical coverages of $\text{H}_2\text{O}_{\text{ads}}$ and $\text{NH}_{3\text{ads}}$ species for 1% $\text{NH}_3/3\%$ $\text{H}_2\text{O}/\text{He}$ considering the competitive Langmuir model. **Inset:** Determining of A_M for the $\delta(\text{H}_2\text{O})$ band using the Langmuir model at 300 K for $P_a = 500$ Pa, 1000 Pa and 2000 Pa.

Figure 3. FTIR spectra recorded during the $\text{NH}_3\text{-H}_2\text{O}$ coadsorption on $\text{SiO}_2\text{-G}$ for 1% $\text{NH}_3/3\%$ $\text{H}_2\text{O}/\text{He}$. **Part A:** Impact of the adsorption duration t_a at $T_a = 300$ K: (a)-(h) $t_a = 10, 23, 66, 78, 101, 121, 155, 202$ s. **Part B:** Impact of T_a the adsorption temperature at the adsorption equilibrium: (a)-(e) $T_a = 300, 313, 335, 373, 453$ in K.

Figure 4. Adsorption of NH_3 and coadsorption of $\text{NH}_3\text{-H}_2\text{O}$ at 300 K on $\text{SiO}_2\text{-A}$ using the M.S system. **Part A:** (I) adsorption of 1% $\text{NH}_3/1\%$ Ar/He and (II) isothermal desorption in helium. **Inset:** NH_3 production during TPD after (II). **Part B:** Coadsorption 1% $\text{NH}_3/2\%$ $\text{H}_2\text{O}/1\%$ Ar/Hr and isothermal desorption on helium. **Inset:** NH_3 and H_2O productions during TPD after II.

Figure 5. Impact of the T_a adsorption temperature on the amount of NH_3 on the $\text{SiO}_2\text{-A}$ surface in the absence (Part A) and in the presence (part B) of H_2O using the TPAE procedure. **Part A:** Evolution of the NH_3 molar fraction during (I) an increase and (II) a decrease in T_a respectively using 1% NH_3 /1% Ar/He. **Part B:** Evolutions of the molar fraction of NH_3 and H_2O during an increase in the adsorption temperature using 1% NH_3 /3% H_2O /1% Ar/He. **Inset:** Comparison of the NH_3 productions in Fig. 5A and 5B during an increase in T_a .

Figure 6. Study of NH_3 adsorption using the TPAE procedure with 1% NH_3 /1% Ar/He. (a): evolution with T_a of the relative molar fraction $(\text{NH}_3(T_a)_{\text{out}} - \text{NH}_3(T_a)_{\text{in}})$ from Fig. 5A part I; blue square symbols: evolution of the average adsorption equilibrium coverage of the $\text{NH}_{3\text{ads}}$ species from curve a; (b) theoretical evolution of the coverage according to the Langmuir model considering the presence of one adsorbed $\text{NH}_{3\text{ads}}$ species with an heat of adsorption of $E_L = 53$ kJ/mol; (c) theoretical evolution of the coverage considering the presence of two adsorbed $\text{NH}_{3\text{ads}1}$ and $\text{NH}_{3\text{ads}2}$ species which obey to the Langmuir ($E_L = 53$ kJ/mol) and Temkin ($E_0 = 72$ kJ/mol, $E_1 = 52$ kJ/mol) adsorption model, respectively with $x_{\text{NH}_{3\text{ads}1}} \approx 0.87$ and $x_{\text{NH}_{3\text{ads}2}} \approx 0.13$ for their respective contribution to the average coverage at 300 K.

Figure 7. Study of NH_3 adsorption using the TPAE procedure with 1% NH_3 /3% H_2O /1% Ar/He. (a): evolution with T_a of the relative molar fraction $(\text{NH}_3(T_a)_{\text{out}} - \text{NH}_3(T_a)_{\text{in}})$ from Fig. 5B; blue square symbols: evolution of the average coadsorption equilibrium coverage of the $\text{NH}_{3\text{ads}}$ species from curve a; (b) theoretical evolution of the coverage according to the Langmuir adsorption model with a heat of adsorption $E_L = 53$ kJ/mol; (c) theoretical evolution of the coverage considering the presence of two adsorbed $\text{NH}_{3\text{ads}1}$ and $\text{NH}_{3\text{ads}2}$ species which obey to the Langmuir ($E_L = 52$ kJ/mol) and Temkin ($E_0 = 74$ kJ/mol, $E_1 = 53$ kJ/mol) adsorption model, respectively with $x_{\text{NH}_{3\text{ads}1}} \approx 0.6$ and $x_{\text{NH}_{3\text{ads}2}} \approx 0.4$ for their respective contribution to the average coverage at 300 K.

TOC Graphic

NH₃ and H₂O coadsorption on SiO₂

Figure1A

765x756mm (96 x 96 DPI)

Figure1B

745x786mm (96 x 96 DPI)

Figure2

962x856mm (96 x 96 DPI)

Figure3A

663x745mm (96 x 96 DPI)

Figure3B

700x729mm (96 x 96 DPI)

Figure4

1599x747mm (96 x 96 DPI)

Figure5

1572x809mm (96 x 96 DPI)

Figure6

902x707mm (96 x 96 DPI)

Figure7

897x737mm (96 x 96 DPI)

NH₃ and H₂O coadsorption on SiO₂

TOC graphic

158x100mm (86 x 86 DPI)